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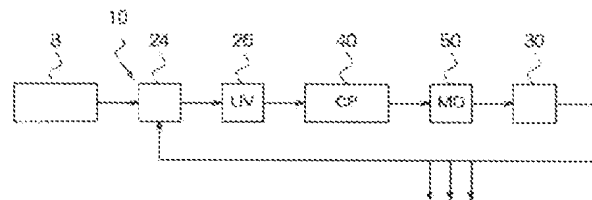
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(54)【発明の名称】 超純水製造装置

(57)【要約】

【課題】 溶存酸素濃度が極めて低く、かつ、溶存窒素を含む全溶存カチオン濃度も大きく低減した超純水を得ることが可能な超純水製造装置を提供する。

【解決手段】 一次純水システム8と二次純水システム10とを備えた超純水製造装置において、二次純水システム10に、紫外線酸化装置26、非再生型イオン交換装置40及び膜脱気装置50をこの順序に通水するように設置する。あるいは、膜脱気装置50の後段にさらに第2の非再生型イオン交換装置を設置する。



【特許請求の範囲】

【請求項1】 一次純水系システムと二次純水系システムとを備えた超純水製造装置において、二次純水系システムに、紫外線酸化装置、非再生型イオン交換装置及び膜脱気装置をこの順序に通水するように設置したことを特徴とする超純水製造装置。

【請求項2】 非再生型イオン交換装置が、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床によるイオン交換装置である請求項1に記載の超純水製造装置。

【請求項3】 非再生型イオン交換装置が、強塩基性陰イオン交換樹脂の単床層を入口側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床層を出口側に設けた複層式イオン交換装置である請求項1に記載の超純水製造装置。

【請求項4】 非再生型イオン交換装置が、強塩基性陰イオン交換樹脂の単床による樹脂塔を前段側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床による樹脂塔を後段側に設けたイオン交換装置である請求項1に記載の超純水製造装置。

【請求項5】 一次純水系システムと二次純水系システムとを備えた超純水製造装置において、二次純水系システムに、紫外線酸化装置、第1の非再生型イオン交換装置、膜脱気装置及び第2の非再生型イオン交換装置をこの順序に通水するように設置したことを特徴とする超純水製造装置。

【請求項6】 第1の非再生型イオン交換装置が、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床によるイオン交換装置である請求項5に記載の超純水製造装置。

【請求項7】 第1の非再生型イオン交換装置が、強塩基性陰イオン交換樹脂の単床によるイオン交換装置である請求項5に記載の超純水製造装置。

【請求項8】 第1の非再生型イオン交換装置が、強塩基性陰イオン交換樹脂の単床層を入口側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床層を出口側に設けた複層式イオン交換装置である請求項5に記載の超純水製造装置。

【請求項9】 第1の非再生型イオン交換装置が、強塩基性陰イオン交換樹脂の単床による樹脂塔を前段側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床による樹脂塔を後段側に設けたイオン交換装置である請求項5に記載の超純水製造装置。

【請求項10】 第2の非再生型イオン交換装置が、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床によるイオン交換装置である請求項5～9に記載の超純水製造装置。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、例えば半導体産業

におけるシリコンウエハの洗浄等に用いられる超純水（純水を含む）の製造装置に関し、さらに詳述すると、二次純水系システムで得られる超純水中の溶存ガス濃度を低減させることができる超純水製造装置に関する。

【0002】

【従来の技術】 シリコンウエハの洗浄等に用いられる超純水の製造装置は、一般に、前処理系システムの処理水が導入される一次純水系システムと、一次純水系システムの処理水が導入される二次純水系システム（サブシステム）とを備えている。このような超純水製造装置としては、例えば図8に示すものが挙げられる。図8において、2は原水貯槽、4は前処理系システム、6は濾過水槽、8は一次純水系システム、10は二次純水系システムを示す。一次純水系システム8には、脱塩装置12、脱塩水槽14、逆浸透膜装置16、逆浸透膜透過水槽18、真空脱気装置20、再生型混床式脱塩装置22が順次設置されている。二次純水系システム10には、純水貯槽24、紫外線酸化装置26、カートリッジポリッシャ28、膜外濾過膜装置30が順次設置されている。

【0003】 図8の装置では、以下の手順で処理が行われる。まず、工業用水等の原水中に含まれる懸濁物質及び有機物の一部が前処理システム4で除去された後、その処理水が濾過水槽6を経て一次純水系システム8に供給され、脱塩装置12、逆浸透膜装置16、真空脱気装置20、再生型混床式脱塩装置22に順次通水される。脱塩装置12は、例えば2床3塔式イオン交換装置等のイオン交換装置であって、水中の不純物イオンの除去を行う。逆浸透膜装置16は、水中の無機イオン、有機物、微粒子等の除去を行う。真空脱気装置20は、水中の溶存酸素等の溶存ガスの除去を行う。再生型混床式脱塩装置22は、残存するイオン等を除去して高純度の純水を製造する。

【0004】 一次純水系システム8の処理水（一次純水）は、二次純水系システム10の純水貯槽24に供給される。純水貯槽24に蓄えられる一次純水は、再生型混床式脱塩装置22によって炭酸ガスが除去されているとともに、真空脱気装置20により酸素ガスが除去されているため、これら酸素ガスや炭酸ガスが外気から再溶解するのを防ぐ目的で、純水貯槽24には不活性ガスである窒素ガスが封入されている。なお、純水貯槽24に蓄えられる一次純水の抵抗率は、通常、 $1\text{M}\Omega \cdot \text{cm}$ 以上である。純水貯槽24を出た純水は、紫外線酸化装置26、カートリッジポリッシャ28、膜外濾過膜装置30に順次通水される。紫外線酸化装置26は、純水貯槽24からの純水に紫外線を照射し、純水中の有機物を酸化分解するとともに、バクテリアの殺菌を行う。カートリッジポリッシャ28は、非再生型混床式イオン交換装置であって、供給されるイオン負荷がほとんどない一次純水中のイオンをさらに除去する。膜外濾過膜装置30は、水中の残存微粒子等を除去して超純水を製造する。

* きたりするおそれがあることによる。

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が再び増加してしまう。紫外線酸化装置 28 における紫外線エールギーは、ヒドロキシラジカルのような極めて反応性に富むラジカルの生成だけではなく、オゾンや過酸化水素のような反応が遅く寿命の長い酸化性物質の生成にも消費されるので、カートリッジポリッシャ 28 で蓄存酸素が再び増加することは避けられない現象である。

【0011】一方、近年、超純水への要求水質として、酸素ガスのみならず窒素ガスを含めた全溶存ガス濃度の低減が求められ始めている。これは、不活性ガスである窒素は、これまで半導体デバイス製造工程への影響はないと考えられてきたが、近年の超音波洗浄装置の導入に伴い、溶存ガスによるキャビテーションが問題となってきたためである。超音波照射時に溶存ガスによるキャビテーションが生じると、超音波エネルギーを無駄に消費してしまう。しかし、図8に示した従来の装置では、真空脱気装置20によって酸素ガスのみならず、窒素ガスや炭酸ガスも含めた全溶存ガスを低減しているが、純水貯槽24において外気を遮断するために封入している窒素ガスが水中に溶解するので、全溶存ガス濃度を低減することは困難であった。

【0012】以上述べたように、従来の超純水製造装置では、紫外線酸化装置におけるオゾンや過酸化水素の生成があるために溶存酸素の低減に限界があるばかりでなく、純水貯槽における封入ガスである窒素ガスの溶解により、全溶存ガス濃度を低減することが困難であった。本発明は、このような事情に鑑みてなされたもので、溶存酸素濃度が極めて低く、かつ、溶存酸素、溶存窒素を含む全溶存ガス濃度も大きく低減した超純水を得ることが可能な超純水製造装置を提供することを目的とする。

【0013】

【課題を解決するための手段】本発明は、前記目的を達成するため、下記第1発明及び第2発明を提供する。

〔第1発明〕一次純水系システムと二次純水系システムとを備えた超純水製造装置において、二次純水系システムに、紫外線酸化装置、非再生型イオン交換装置及び膜脱気装置をこの順序に通水するように設置したことを特徴とする超純水製造装置。

〔第2発明〕一次純水系システムと二次純水系システムとを備えた超純水製造装置において、二次純水系システムに、紫外線酸化装置、第1の非再生型イオン交換装置、膜脱気装置及び第2の非再生型イオン交換装置をこの順序に通水するように設置したことを特徴とする超純水製造装置。

【0014】第1発明及び第2発明の超純水製造装置では、二次純水系システムにおいて、紫外線酸化装置の後段の非再生型イオン交換装置の後段に膜脱気装置を設置したことにより、紫外線酸化装置で生成したオゾンや過酸化水素が後段の非再生型イオン交換装置でイオン交換樹脂と接触して分解し、これにより溶存酸素が増加しても、この溶存酸素を後段の膜脱気装置で除去して、溶存酸素濃度が極めて低い超純水を得ることができる。また、膜脱気装置の入口水に溶存酸素等の溶存酸素以外の溶存ガスが含まれている場合でも、この溶存酸素以外の溶存ガスを膜脱気装置で除去して、全溶存ガス濃度が大きく低減した超純水を得ることができる。さらに、第2発明の超純水製造装置では、膜脱気装置の後段にさらに第2の非再生型イオン交換装置を設けたので、この第2の非再生型イオン交換装置により、膜脱気装置から溶出した不純物を含めて水中の不純物をほぼ完全に除去することができる。

【0015】本発明において、一次純水系システムとは、前処理システムによって懸濁物質、有機物の一部等が除去された水が導入され、その水の中のイオン、非イオン性物質、溶存ガス等の大部分を除去して一次純水を得るシステムをいう。また、二次純水系システムとは、一次純水が導入され、一次純水中に残存する微量の不純物を取り除くものである。二次純水系システムでは連続循環運転を行っており、得られた超純水の一部をユースポイントに送るとともに、残部を純水貯槽に循環している。

【0016】本発明では、二次純水系システムにおいて、前段側から後段側にかけて紫外線酸化装置、非再生型イオン交換装置及び膜脱気装置を設置するか（第1発明）、紫外線酸化装置、第1の非再生型イオン交換装置、膜脱気装置及び第2の非再生型イオン交換装置を設置する（第2発明）。なお、以下の説明において第1の非再生型イオン交換装置という場合、該用語は、第1発明における紫外線酸化装置と膜脱気装置との間の非再生型イオン交換装置及び第2発明における第1の非再生型

イオン交換装置の両方を意味することがある。

【0017】紫外線酸化装置としては、被処理水に少なくとも254nm付近の波長の紫外線を照射可能な紫外線ランプを備え、被処理水中の有機物を分解可能なものを用いる。紫外線ランプとしては、一般に低圧水銀ランプが用いられる。また、紫外線酸化装置としては、流通型、浸漬型といった任意の構成のものを用いることができるが、流通型紫外線酸化装置を用いることが処理効率等の点で適当である。

【0018】紫外線酸化装置には、254nm付近の波長の紫外線に加えて、それより高い有機物分解能力がある185nm付近の波長の紫外線も照射可能な装置がある。さらに、その中でも、185nm付近の波長の紫外線の照射量が少ない紫外線酸化装置と、185nm付近の波長の紫外線を強く照射可能な紫外線酸化装置とがある。前者の装置は、有機物分解能力が低いため、後者の装置と区別して紫外線殺菌装置と呼ばれることもある。本発明では、254nm付近の波長の紫外線に加え、185nm付近の波長の紫外線も強く照射可能な後者の紫外線酸化装置を用いることが、有機物を良好に分解する点で好ましい。

【0019】第1の非再生型イオン交換装置（第1発明における紫外線酸化装置と膜脱気装置との間の非再生型イオン交換装置を含む）としては、必ずしも限定されないが、例えば下記①～④のものが用いることができる。

①～③は1塔式、④は2塔式のイオン交換装置である。
①強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床によるイオン交換装置。

②強塩基性陰イオン交換樹脂の単床によるイオン交換装置。

③強塩基性陰イオン交換樹脂の単床層を入口側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床層を出口側に設けた複層式イオン交換装置。

④強塩基性陰イオン交換樹脂の単床による樹脂塔を前段側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床による樹脂塔を後段側に設けたイオン交換装置。

【0020】第1の非再生型イオン交換装置として③のイオン交換装置を用いた場合には、混床層内のいずれの位置においても水のpHの変化がないため、効率の良いイオン交換ができるという利点を得られる。また、オゾンや過酸化水素のような酸化性物質が強酸性陽イオン交換樹脂に接触すると、強酸性陽イオン交換樹脂から溶出物が発生し、それが強酸性陽イオン交換樹脂や強塩基性陰イオン交換樹脂の表面を汚染して、イオン交換速度が低下することがある。一方、オゾンや過酸化水素の分解は、強塩基性陰イオン交換樹脂に接触させるだけで十分に行われる。したがって、第1の非再生型イオン交換装置としては、②～④のイオン交換装置のようにイオン交換樹脂層の少なくとも入口側又はイオン交換樹脂層の全

部が強塩基性陰イオン交換樹脂の単床であるものを用いることが特に好ましい。これにより、オゾンや過酸化水素を強酸性陽イオン交換樹脂と接触させることなく強塩基性陰イオン交換樹脂で分解することが可能となり、強酸性陽イオン交換樹脂から溶出物を発生させることなくオゾンや過酸化水素を分解できるという利点が得られる。ただし、第1の非再生型イオン交換装置として強塩基性陰イオン交換樹脂の単床による②のイオン交換装置を用いた場合には、不純物の除去の点で膜脱気装置の後段に強酸性陽イオン交換樹脂を含む第2の非再生型イオン交換装置を設けることが適当である。

【0021】膜脱気装置とは、気体分離膜で仕切られた一方の室に被処理水を流すとともに、他方の室を減圧することにより、被処理水中に含まれるガスを気体分離膜を通して他方の室に移行させて除去する装置である。気体分離膜としては、通常、テトラフルオロエチレン系、シリコンゴム系等の疎水性の高分子膜を中空糸膜状等の適宜形状に形成したものが使用される。本発明において、膜脱気装置としては、水中の溶存酸素濃度を1ppb以下、全溶存ガス濃度を3000ppb以下に低減できるものが好ましい。なお、本発明において脱ガス装置として膜脱気装置を用いたのは、真空脱気塔や加熱脱気装置等の脱ガス装置を用いた場合には、これらの装置から水中に不純物が混入したり、装置の充填物から水中に不純物が溶出したりすることがある上、装置が大型化するからである。これに対し、膜脱気装置を用いれば、このような問題は生じない。

【0022】第2の非再生型イオン交換装置としては、必ずしも限定されないが、前述した①の強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床によるイオン交換装置を用いることが適当であり、これにより混床層内のいずれの位置においても水のpHの変化がないため効率の良いイオン交換ができるという利点を得ることができる。

【0023】また、第2発明では、第1の非再生型イオン交換装置の通水SV（空間速度）（SV1）と、第2の非再生型イオン交換装置の通水SV（SV2）が、 $SV1 < SV2$ の関係にあることが好ましい。これは、紫外線酸化装置の処理水を第1の非再生型イオン交換装置に比較的接触時間を大として通過させることにより、紫外線酸化で生成したオゾン、過酸化水素等を十分に分解したのちに膜脱気装置で処理することが望ましいという理由からである。

【0024】

【発明の実施の形態】図1～図3はそれぞれ第1発明に係る超純水製造装置の一実施形態例を示すフロー図。図4～図7はそれぞれ第2発明に係る超純水製造装置の一実施形態例を示すフロー図である。図1～図7において、図8の装置と同一の構成部分には同一参照符号を付してその説明を省略する。また、図1～図7において、

前処理系システムは図示を省略し、一次純水系システム8は図示を簡略化してある。

【0025】図1の装置は、二次純水系システム10に、紫外線酸化装置26（図中UVで示す）と、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床による1塔式の非再生型イオン交換装置40（図中CPで示す）と、膜脱気装置50（図中MDで示す）とをこの順序に通水するように設置したものである。

【0026】図2の装置は、図1の装置において、非再生型イオン交換装置40に代えて、強塩基性陰イオン交換樹脂の単床層（図中AERで示す）を入口側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床層（図中MBで示す）を出口側に設けた1塔式の非再生型イオン交換装置42を設置したものである。

【0027】図3の装置は、図1の装置において、非再生型イオン交換装置40に代えて、強塩基性陰イオン交換樹脂の単床による樹脂塔44（図中AERで示す）を前段側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床による樹脂塔46（図中MBで示す）を後段側に設けた2塔式の非再生型イオン交換装置48を設置したものである。

【0028】図4の装置は、二次純水系システム10に、紫外線酸化装置26（図中UVで示す）と、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床による1塔式の第1の非再生型イオン交換装置40（図中CPで示す）と、膜脱気装置50（図中MDで示す）と、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床による1塔式の第2の非再生型イオン交換装置60（図中CPで示す）とをこの順序に通水するように設置したものである。

【0029】図5の装置は、図4の装置において、第1の非再生型イオン交換装置40に代えて、強塩基性陰イオン交換樹脂の単床による1塔式のイオン交換装置70（図中APで示す）を設置したものである。

【0030】図6の装置は、図4の装置において、第1の非再生型イオン交換装置40に代えて、強塩基性陰イオン交換樹脂の単床層（図中AERで示す）を入口側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床層（図中MBで示す）を出口側に設けた1塔式の非再生型イオン交換装置42を設置したものである。

【0031】図7の装置は、図4の装置において、第1の非再生型イオン交換装置40に代えて、強塩基性陰イオン交換樹脂の単床による樹脂塔44（図中AERで示す）を前段側、強酸性陽イオン交換樹脂と強塩基性陰イオン交換樹脂との混床による樹脂塔46（図中MBで示す）を後段側に設けた非再生型イオン交換装置48を設置したものである。

【0032】なお、図1～図7の装置において、紫外線酸化装置とその後段の非再生型イオン交換装置との間、該非再生型イオン交換装置とその後段の膜脱気装置との

間、該膜脱気装置とその後段の非再生型イオン交換装置との間には、必要に応じ、他の装置を設置してもよい。

【0033】

【実施例】図1～図7に示した超純水製造装置の各ポイントにおける水中の溶存酸素濃度、溶存窒素濃度及び抵抗率を測定した。この場合、各装置として下記のものを用い、処理条件は下記の通りとした。また、溶存酸素濃度の測定には東亜電機社製DO-30Aを用い、抵抗率の測定にはオルガン（株）製MH-4を用いた。結果を表2～8に示す。なお、図1～7に示した超純水製造装置において、一次純水システム8の脱塩装置12及び真空脱気装置20（図8参照）の出口水の溶存酸素濃度は、それぞれ8.0ppm、2.4ppbであった。

【0034】装置

・紫外線酸化装置26：TDFL-4（千代田工業社製）
・イオン交換装置40：アンバーライトIRA-402 BL（ローランドハース社製）

*

・イオン交換装置42：アンバーライトIRA-402 BL + アンバーライトEG-4
・イオン交換装置48：アンバーライトIRA-402 BL、アンバーライトEG-4
・イオン交換装置70：アンバーライトIRA-402 BL
・膜脱気装置50：MJ-620p（大日本インキ化学工業（株）製）
・イオン交換装置60：アンバーライトEG-4
【0035】処理条件
・紫外線酸化装置26における紫外線照射量：0.3Kw・hr/m²
・イオン交換装置40、42、48、70における通水SV：50hr⁻¹
・膜脱気装置50における真空度：25Torr
・イオン交換装置50における通水SV：120hr⁻¹
【0036】
【表2】

図1の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppm)	抵抗率 (MΩ・cm)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	0	1.2	17.5
イオン交換装置(40)出口	1.0	1.2	18.2
膜脱気装置(50)出口	<1	<2	18.1

【表3】

図2の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppm)	抵抗率 (MΩ・cm)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	0	1.2	17.5
イオン交換装置(42)出口	1.0	1.2	18.2
膜脱気装置(50)出口	<1	<2	18.1

【表4】

図3の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppm)	抵抗率 (MΩ・cm)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	0	1.2	17.5
イオン交換装置(48)出口	1.0	1.2	18.2
膜脱気装置(50)出口	<1	<2	18.1

【表5】

図4の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppm)	抵抗率 (MΩ・cm)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	0	1.2	17.5
イオン交換装置(49)出口	1.0	1.2	18.2
膜脱気装置(50)出口	<1	<2	18.1
イオン交換装置(50)出口	<1	<2	18.2

【表6】

図5の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppb)	抵抗率 ($\text{M}\Omega \cdot \text{cm}$)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(70)出口	1.0	1.2	18.0
膜脱気装置(50)出口	<1	<2	17.9
イオン交換装置(80)出口	<1	<2	18.2

【表7】

図6の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppb)	抵抗率 ($\text{M}\Omega \cdot \text{cm}$)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(42)出口	1.0	1.2	18.2
膜脱気装置(50)出口	<1	<2	18.1
イオン交換装置(80)出口	<1	<2	18.2

【表8】

図7の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppb)	抵抗率 ($\text{M}\Omega \cdot \text{cm}$)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(48)出口	1.0	1.2	18.2
膜脱気装置(50)出口	<1	<2	18.1
イオン交換装置(80)出口	<1	<2	18.2

【0037】表2～表8より、第1発明及び第2発明によれば、溶存酸素濃度及び溶存窒素濃度がいずれも極めて低い超純水を得ることができることがわかる。また、第2発明によれば、不純物がほぼ完全に除去された超純水を得ることができることがわかる。

【0038】

【発明の効果】以上説明したように、第1発明及び第2発明の超純水製造装置によれば、溶存酸素濃度が極めて低く、かつ、溶存酸素、溶存窒素を含む全溶存ガス濃度も大きく低減した超純水を得ることができる。また、第2発明の超純水製造装置によれば、不純物がより低減した超純水を得ることができる。

【図面の簡単な説明】

【図1】第1発明に係る超純水製造装置の一実施形態例を示すフロー図である。

【図2】第1発明に係る超純水製造装置の一実施形態例を示すフロー図である。

【図3】第1発明に係る超純水製造装置の一実施形態例を示すフロー図である。

【図4】第2発明に係る超純水製造装置の一実施形態例を示すフロー図である。

*【図5】第2発明に係る超純水製造装置の一実施形態例を示すフロー図である。

【図6】第2発明に係る超純水製造装置の一実施形態例を示すフロー図である。

【図7】第2発明に係る超純水製造装置の一実施形態例を示すフロー図である。

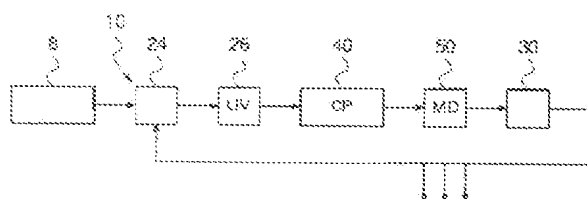
【図8】従来の超純水製造装置の一例を示すフロー図である。

【符号の説明】

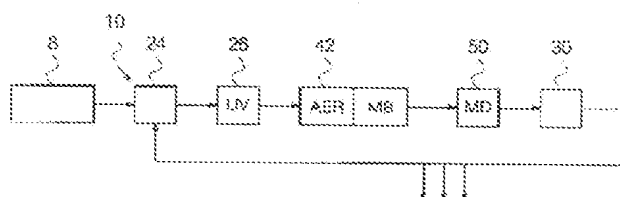
- 8 一次純水系システム
- 10 二次純水系システム
- 24 純水貯槽
- 26 紫外線酸化装置
- 30 限外濾過膜装置
- 40 第1の非再生型イオン交換装置
- 42 第1の非再生型イオン交換装置
- 48 第1の非再生型イオン交換装置
- 50 膜脱気装置
- 60 第2の非再生型イオン交換装置
- 70 第1の非再生型イオン交換装置

*

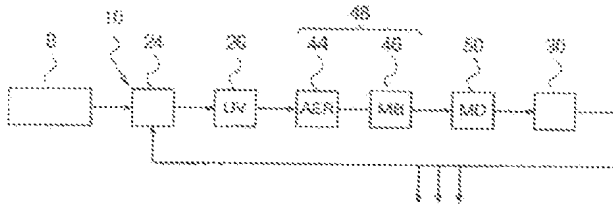
【図1】



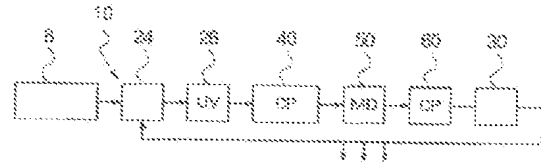
【図2】



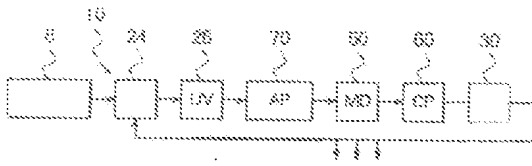
【図3】



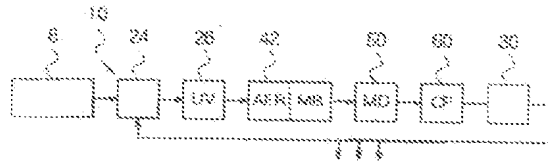
【図4】



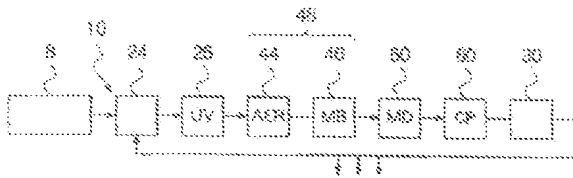
【図5】



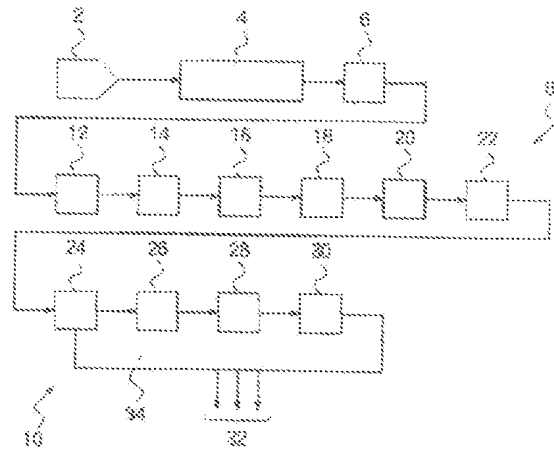
【図6】



【図7】



【図8】



PATENT ABSTRACTS OF JAPAN

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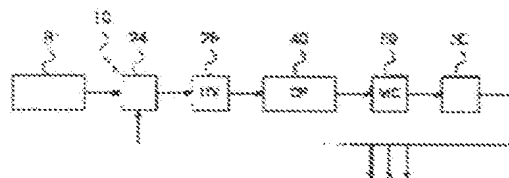
(22)Date of filing : 19.08.1996 (72)Inventor : TANABE MADOKA

(54) PRODUCTION DEVICE OF ULTRAPURE WATER

(57)Abstract:

PROBLEM TO BE SOLVED: To produce an ultrapure water reduced in dissolved gas concentration such as dissolved oxygen concentration by arranging in order an ultraviolet oxidizing device, a non-regenerative ion exchange device and a membrane deaerating device in the secondary pure water system in the ultrapure water production device provided with a primary pure water system and the secondary pure water system.

SOLUTION: A primary pure water system 8 and a secondary pure water system 10 are arranged in the device producing the ultrapure water used for washing, etc., of a silicon wafer. In this case, the secondary pure water system 10 is constituted by arranging in order a pure water storage tank 24, the ultraviolet oxidizing device 26, the one tower system non-regenerative ion exchange device 40 consisting of a mixed bed of a strongly acidic cation exchange resin and a strongly basic anion exchange resin, the membrane deaerating device 50 and an ultrafilter membrane device 30. In this way, the ultrapure water very low in dissolved oxygen concentration is obtained by allowing an ozone and hydrogen peroxide formed at the ultraviolet oxidizing device 26 to bring into contact with the ion exchange resin at the non-regenerative ion exchange device to decompose and remove the dissolved oxygen with the membrane deaerating device 50 even if the dissolved oxygen is increased.



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registration]
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CLAIMS

[Claim(s)]

- [Claim 1] Ultrapure water equipments characterized by installing ultraviolet ray oxidation equipment, a non-reproducing mold ion exchange unit, and a film deaerator in a secondary pure-water system so that it may let water flow in this sequence in ultrapure water equipments equipped with the primary pure drainage system system and the secondary pure-water system.
- [Claim 2] Ultrapure water equipments according to claim 1 whose non-reproducing mold ion exchange unit is an ion exchange unit by the mixed bed of strongly acidic cation exchange resin and strongly basic anion exchange resin.
- [Claim 3] Ultrapure water equipments according to claim 1 whose non-reproducing mold ion exchange unit is a double layer type ion exchange unit which prepared the entrance side and the mixed bed layer of strongly acidic cation exchange resin and strongly basic anion exchange resin for the single flooring layer of strongly basic anion exchange resin in the outlet side.
- [Claim 4] resin according [a non-reproducing mold ion exchange unit] to the single flooring of strongly basic anion exchange resin --- resin according a column to the mixed bed of a preceding paragraph side, strongly acidic cation exchange resin, and strongly basic anion exchange resin --- the ultrapure water equipments according to claim 1 which are ion exchange units which established the column in the latter-part side.
- [Claim 5] Ultrapure water equipments characterized by installing ultraviolet ray oxidation equipment, the 1st non-reproducing mold ion exchange unit, a film deaerator, and the 2nd non-reproducing mold ion exchange unit in a secondary pure-water system so that it may let water flow in this sequence in ultrapure water equipments equipped with the primary pure drainage system system and the secondary pure-water system.
- [Claim 6] Ultrapure water equipments according to claim 5 whose 1st non-reproducing mold ion exchange unit is an ion exchange unit by the mixed bed of strongly acidic cation exchange resin and strongly basic anion exchange resin.
- [Claim 7] Ultrapure water equipments according to claim 5 whose 1st non-reproducing mold ion exchange unit is an ion exchange unit by the single flooring of strongly basic anion exchange resin.
- [Claim 8] Ultrapure water equipments according to claim 5 whose 1st non-reproducing mold ion exchange unit is a double layer type ion exchange unit which prepared the entrance side and the mixed bed layer of strongly acidic cation exchange resin and strongly basic anion exchange resin for the single flooring layer of strongly basic anion exchange resin in the outlet side.
- [Claim 9] resin according [the 1st non-reproducing mold ion exchange unit] to the single flooring of strongly basic anion exchange resin --- resin according a column to the mixed bed of a preceding paragraph side, strongly acidic cation exchange resin, and strongly basic anion exchange resin --- the ultrapure water equipments according to claim 5 which are ion exchange units which established the column in the latter-part side.
- [Claim 10] Ultrapure water equipments according to claim 5 to 9 whose 2nd non-reproducing mold ion exchange unit is an ion exchange unit by the mixed bed of strongly acidic cation exchange resin and strongly basic anion exchange resin.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] When this invention is further explained in full detail about the manufacturing installation of the ultrapure water (pure water is included) used for washing of the silicon wafer in semiconductor industry etc., it relates to the ultrapure water equipments which can reduce the dissolved gas concentration in the ultrapure water obtained by the secondary pure-water system.

[0002]

[Description of the Prior Art] Generally the manufacturing installation of the ultrapure water used for washing of a silicon wafer etc. is equipped with the primary pure drainage system system by which the treated water of a preprocessor system is introduced, and the secondary pure-water system (subsystem) by which the treated water of a primary pure drainage system system is introduced. As such ultrapure water equipments, what is shown, for example in drawing 8 is mentioned. In drawing 8, in 2, a filtered water tub and 8 show a primary pure drainage system system, and, as for a raw water tank and 4, 10 shows a secondary pure-water system, as for a preprocessor system and 6. Sequential installation of a demineralizer 12, the desalted water tub 14, reverse osmotic membrane equipment 16, the reverse osmotic membrane permeated water tub 18, vacuum deairing equipment 20, and the playback mold mixed-bed-deionization equipment 22 is carried out at the primary pure drainage system system 8. Sequential installation of the pure-water tank 24, ultraviolet ray oxidation equipment 26, a cartridge polisher 28, and the ultrafiltration membrane equipment 30 is carried out at the secondary pure-water system 10.

[0003] Processing is performed by the following procedures with the equipment of drawing 8. First, after some of suspended solids contained in raw water, such as industrial water, and organic substance are removed by the pretreatment system 4, the treated water is supplied to the primary pure drainage system system 8 through the filtered water tub 6, and sequential water flow is carried out at a demineralizer 12, reverse osmotic membrane equipment 16, vacuum deairing equipment 20, and playback mold mixed-bed-deionization equipment 22. 2 floors, demineralizers 12 are ion exchange units, such as a type ion exchange unit, 3 column, and remove underwater impurity ion, for example. Reverse osmotic membrane equipment 16 removes underwater inorganic ion, the organic substance,

a particle, etc. Vacuum deairing equipment 20 removes dissolved gas, such as underwater dissolved oxygen. Playback mold mixed-bed-deionization equipment 22 removes the ion which remains, and manufactures the pure water of a high grade. [0004] The treated water (primary pure water) of the primary pure drainage system 8 is supplied to the pure-water tank 24 of the secondary pure-water system 10. It is the purpose which prevents these oxygen gas and carbon dioxide gas remelting the primary pure water stored in the pure-water tank 24 from the open air since oxygen gas is removed by vacuum deairing equipment 20 while carbon dioxide gas is removed by playback mold mixed-bed-deionization equipment 22, and the nitrogen gas which is inert gas is enclosed with the pure-water tank 24. In addition, the resistivity of the primary pure water stored in the pure-water tank 24 is usually 1 or more M omega-cm. The sequential water flow of the pure water which came out of the pure-water tank 24 is carried out at ultraviolet ray oxidation equipment 26, a cartridge polisher 28, and ultrafiltration membrane equipment 30. Ultraviolet ray oxidation equipment 26 sterilizes bacteria while it irradiates ultraviolet rays from the pure-water tank 24 at pure water and understands the organic substance in pure water an oxidized part. A cartridge polisher 28 is a non-reproducing mold mixed bed type ion exchange unit, and removes further the primary pure underwater ion which does not almost have the ion load supplied. Ultrafiltration membrane equipment 30 removes an underwater residual particle etc., and manufactures ultrapure water. The obtained ultrapure water is supplied to a service space 32.

[0005] Moreover, ultrapure water always circulates through the inside of the closed loop which becomes the pure-water tank 24 from return and the pure-water tank 24 -> ultraviolet-ray-oxidation-equipment 26 -> cartridge polisher 28 -> ultrafiltration membrane equipment 30 -> ultrapure water circulation piping 34 -> pure-water tank 24 through the secondary pure-water circulation piping 34 in any [at which it is used in the service space 32 / when not using it at the time] case. Thus, always circulating ultrapure water If operation is suspended at the time of un-using [of the ultrapure water in a service space 32] it, water will pile up into each unit which constitutes a system, or piping at the time of shutdown. Growth of bacteria breaks out or It is because there is a possibility that a particle may be breathed out from each unit with the shock at the time of that there is a possibility of an ion component and the organic substance being eluted with a minute amount, and degrading the water quality of ultrapure water, a halt, and a reboot, or the elution of an impurity may occur.

[0006]

[Problem(s) to be Solved by the Invention] Although the ultrapure water of a high grade is extremely manufactured by equipment which was mentioned above, in connection with the high integration of a semiconductor device in recent years, making ultrapure water into still higher water quality is called for. Especially dissolved oxygen generates the natural oxidation film on a silicon wafer, and in order to cause the problem of increase of contact resistance, and the problem of causing trouble to the thickness control of a thin oxide film etc. depending on the case, all possible reduction is called for.

[0007] Table 1 shows the measured value of the dissolved oxygen concentration in

each point of the conventional equipment shown in drawing 8. Table 1 shows the following things.

[Table 1]

測定ポイント	溶解酸素濃度
脱塩装置(12)出口	8.0 ppb
真空脱気装置(20)出口	2.4 ppb
純水貯槽(24)出口	2.2 ppb
紫外線酸化装置(26)出口	6 ppb
カートリッジポリッシャー(28)出口	1.0 ppb

Although the dissolved oxygen of saturated concentration is mostly detected by the outlet underwater of a demineralizer 12, it is removed by vacuum deairing equipment 20 to 24ppb. It is set to 22ppb by minding the pure-water tank 24 after that. Reduction of the dissolved oxygen in the pure-water tank 24 is considered to be because for the nitrogen gas which is enclosed with water within the pure-water tank 24 in addition to the low water of dissolved oxygen concentration being supplied from the ultrapure water circulation piping 34 to contact.

[0008] The primary pure water picked out from the pure-water tank 24 is processed with ultraviolet ray oxidation equipment 26. ultraviolet ray oxidation equipment 26 — the ultraviolet rays of the wavelength near 254nm — the organic substance higher than it — resolution — it is ultraviolet ray oxidation equipment equipped with the low-pressure mercury lamp which the ultraviolet rays near [powerful] 185nm can also be strong, and can irradiate them, and it is installed in order to disassemble the underwater organic substance into carbonic acid or an organic acid. The phenomenon in which dissolved oxygen concentration decreases sharply from 22ppb to 6ppb before and behind ultraviolet ray oxidation equipment 26 is accepted as shown in Table 1. This phenomenon is considered because it is consumed as a source of oxygen for oxidization of the processed underwater dissolved oxygen of ultraviolet ray oxidation equipment 26 of the organic substance or is consumed by generation of the radical by the interaction of ultraviolet rays and water, ozone, a hydrogen peroxide, etc.

[0009] However, at the outlet of a cartridge polisher 28, the dissolved oxygen which was decreasing to 6ppb has increased to 10ppb. Since ozone and the hydrogen peroxide which were generated with ultraviolet ray oxidation equipment 26 decomposed into oxygen gas by contact on the ion exchange resin of a cartridge polisher 28, the increment in this dissolved oxygen is presumed.

[0010] As mentioned above, with conventional equipment, although dissolved oxygen concentration underwater with the ultraviolet ray oxidation equipment 26 of the secondary pure-water system 10 decreases greatly, dissolved oxygen will increase again by contact on the ion exchange resin in the latter cartridge polisher 28. That dissolved oxygen increases again the ultraviolet-rays energy in ultraviolet ray oxidation equipment 26 with a cartridge polisher 28 since not only generation of a radical like a hydroxy radical which is extremely rich in reactivity but a reaction like ozone or a hydrogen peroxide is consumed by generation of the late long oxidizer of a life is a phenomenon which is not avoided.

[0011] On the other hand, reduction of total dissolved gas concentration not only including oxygen gas but nitrogen gas is beginning to be called for as demand water quality to ultrapure water in recent years. Although the nitrogen this [whose] is

inert gas has so far been considered that there is no effect on a semiconductor device production process, it is because the cavitation by dissolved gas has posed a problem with installation of an ultrasonic cleaner in recent years. If the cavitation by dissolved gas arises at the time of ultrasonic irradiation, ultrasonic energy will be consumed vainly. However, although all the dissolved gas that includes not only oxygen gas but nitrogen gas and carbon dioxide gas with vacuum deairing equipment 20 was reduced with the conventional equipment shown in drawing 8, since the nitrogen gas enclosed in order to intercept the open air in the pure-water tank 24 dissolved underwater, it was difficult [it] to reduce total dissolved gas concentration.

[0012] As stated above, since there was generation of the ozone in ultraviolet ray oxidation equipment or a hydrogen peroxide in the conventional ultrapure water equipments, it was difficult a limitation to be not only in reduction of dissolved oxygen, but to reduce total dissolved gas concentration by the dissolution of the nitrogen gas which is filler gas in a pure-water tank. This invention was made in view of such a situation, and its dissolved oxygen concentration is very low, and it also aims the total dissolved gas concentration containing dissolved oxygen and dissolved nitrogen at offering the ultrapure water equipments which can obtain the ultrapure water reduced greatly.

[0013]

[Means for Solving the Problem] This invention offers the 1st invention of the following, and the 2nd invention in order to attain said purpose.

Ultrapure water equipments characterized by installing ultraviolet ray oxidation equipment, a non-reproducing mold ion exchange unit, and a film deaerator in a secondary pure-water system so that it may let water flow in this sequence in ultrapure water equipments equipped with the [1st invention] primary pure drainage system system and the secondary pure-water system.

Ultrapure water equipments characterized by installing ultraviolet ray oxidation equipment, the 1st non-reproducing mold ion exchange unit, a film deaerator, and the 2nd non-reproducing mold ion exchange unit in a secondary pure-water system so that it may let water flow in this sequence in ultrapure water equipments equipped with the [2nd invention] primary pure drainage system system and the secondary pure-water system.

[0014] In the ultrapure water equipments of the 1st invention and the 2nd invention In a secondary pure-water system, by having installed the film deaerator in the latter part of the non-reproducing mold ion exchange unit of the latter part of ultraviolet ray oxidation equipment Even if ozone and the hydrogen peroxide which were generated with ultraviolet ray oxidation equipment contact ion exchange resin, and decompose with a latter non-reproducing mold ion exchange unit and dissolved oxygen increases by this, a latter film deaerator can remove this dissolved oxygen, and dissolved oxygen concentration can obtain very low ultrapure water. Moreover, even when dissolved gas other than dissolved oxygen, such as dissolved nitrogen, is contained in the inlet-port water of a film deaerator, a film deaerator can remove dissolved gas other than this dissolved oxygen, and the ultrapure water which total dissolved gas concentration reduced greatly can be obtained. Furthermore, in the ultrapure water equipments of the 2nd invention,

since the 2nd non-reproducing mold ion exchange unit was further formed in the latter part of a film deaerator, this 2nd non-reproducing mold ion exchange unit can remove nearly completely underwater impurities including the impurity eluted from the film deaerator.

[0015] In this invention, the water from which some of suspended solids and organic substance were removed by the pretreatment system is introduced, and a primary pure drainage system system means the system which removes most, such as ion in the water, nonionic matter, and dissolved gas, and obtains primary pure water. Moreover, primary pure water is introduced and a secondary pure-water system removes the impurity of the minute amount which remains in primary pure underwater one. In the secondary pure-water system, continuation circulation operation is performed, and while sending some obtained ultrapure water to the point of use, it circulates through the remainder to the pure-water tank.

[0016] In this invention, in a secondary pure-water system, it applies to a latter-part side from a preceding paragraph side, and ultraviolet ray oxidation equipment, a non-reproducing mold ion exchange unit, and a film deaerator are installed, or (the 1st invention) ultraviolet ray oxidation equipment, the 1st non-reproducing mold ion exchange unit, a film deaerator, and the 2nd non-reproducing mold ion exchange unit are installed (the 2nd invention). In addition, when calling it the 1st non-reproducing mold ion exchange unit in the following explanation, this vocabulary may mean both the non-reproducing mold ion exchange unit between the ultraviolet ray oxidation equipment and the film deaerators in the 1st invention, and the 1st non-reproducing mold ion exchange unit in the 2nd invention.

[0017] Processed water is equipped with the ultraviolet ray lamp which can irradiate the ultraviolet rays of the wavelength near at least 254nm as ultraviolet ray oxidation equipment, and what can disassemble the processed underwater organic substance is used. Generally as an ultraviolet ray lamp, a low-pressure mercury lamp is used. Moreover, although the thing of the configuration of arbitration, such as a circulation mold and a dipping former, can be used as ultraviolet ray oxidation equipment, it is appropriate to use circulation mold ultraviolet ray oxidation equipment in respect of processing effectiveness etc.

[0018] ultraviolet ray oxidation equipment --- the ultraviolet rays of the wavelength near 254nm --- in addition, the organic substance higher than it --- resolution --- there is equipment which can also irradiate the ultraviolet rays of the wavelength near [powerful] 185nm. Furthermore, there is powerful ultraviolet ray oxidation equipment which can be irradiated also in it about the ultraviolet rays of ultraviolet ray oxidation equipment with few exposures of the ultraviolet rays of the wavelength near 185nm, and the wavelength near 185nm. Since the former equipment has low organic substance decomposition capacity, in distinction from the latter equipment, it may be called a ultraviolet water sterilizer. It is desirable to use the ultraviolet ray oxidation equipment of the latter which the ultraviolet rays of the wavelength near 185nm can also be strong, and can irradiate them at this invention in addition to the ultraviolet rays of the wavelength near 254nm at the point which disassembles the organic substance good.

[0019] As 1st non-reproducing mold ion exchange unit (the non-reproducing mold ion exchange unit between the ultraviolet ray oxidation equipment and the film

deaerators in the 1st invention is included), although not necessarily limited, the thing of the following ** - ** can use, for example, ** - 1 column, ** is a type and ** is the ion exchange unit of a type 2 columns.

** The ion exchange unit by the mixed bed of strongly acidic cation exchange resin and strongly basic anion exchange resin.

** The ion exchange unit by the single flooring of strongly basic anion exchange resin.

** The double layer type ion exchange unit which prepared the entrance side and the mixed bed layer of strongly acidic cation exchange resin and strongly basic anion exchange resin for the single flooring layer of strongly basic anion exchange resin in the outlet side.

** the resin by the single flooring of strongly basic anion exchange resin --- resin according a column to the mixed bed of a preceding paragraph side, strongly acidic cation exchange resin, and strongly basic anion exchange resin --- the ion exchange unit which established the column in the latter-part side.

[0020] Since there is no change of pH of water also in which location in a mixed bed layer when the ion exchange unit of ** is used as 1st non-reproducing mold ion exchange unit, the advantage that the efficient ion exchange is made is acquired. Moreover, when an oxidizing substance like ozone or a hydrogen peroxide contacts strongly acidic cation exchange resin, an effluent may be generated from strongly acidic cation exchange resin, it may pollute the front face of strongly acidic cation exchange resin or strongly basic anion exchange resin, and an ion-exchange rate may fall. On the other hand, disassembly of ozone or a hydrogen peroxide is fully performed only by making strongly basic anion exchange resin contact. Therefore, especially the thing for which the thing of an ion-exchange-resin layer whose all of an entrance side or ion-exchange-resin layers are the single floorings of strongly basic anion exchange resin at least is used like the ion exchange unit of ** - ** as 1st non-reproducing mold ion exchange unit is desirable. It becomes possible to decompose with strongly basic anion exchange resin by this, without contacting ozone and a hydrogen peroxide to strongly acidic cation exchange resin, and the advantage that ozone and a hydrogen peroxide can be disassembled is acquired, without generating an effluent from strongly acidic cation exchange resin. However, when the ion exchange unit of ** by the single flooring of strongly basic anion exchange resin is used as 1st non-reproducing mold ion exchange unit, it is appropriate to form the 2nd non-reproducing mold ion exchange unit containing strongly acidic cation exchange resin in the latter part of a film deaerator in respect of removal of an impurity.

[0021] A film deaerator is equipment from which the gas contained in processed underwater one is made to shift to ** of another side through gas permeation membrane, and is removed by decompressing ** of another side while while was divided with gas permeation membrane and it pours processed water to ** by it. As gas permeation membrane, what formed [shape / of a hollow fiber] suitably hydrophobic poly membranes, such as a tetrafluoroethylene system and a silicone rubber system, in the configuration is usually used. In this invention, what can reduce 1 or less ppb and total dissolved gas concentration for underwater dissolved oxygen concentration to 3000 or less ppb is desirable as a film deaerator.

In addition, when degassing apparatus, such as a vacuum degasifier and heat deairing equipment, were used, an impurity may have mixed underwater from these equipments or an impurity may have been underwater eluted from packing of equipment, in this invention, the film deaerator was used as degassing apparatus because equipment was enlarged. On the other hand, such a problem will not be produced if a film deaerator is used.

[0022] As 2nd non-reproducing mold ion exchange unit, although not necessarily limited, it is appropriate to use the ion exchange unit by the mixed bed of the strongly acidic cation exchange resin of ** and strongly basic anion exchange resin which were mentioned above, and since there is no change of pH of water also in which location in a mixed bed layer by this, the advantage that the efficient ion exchange is made can be acquired.

[0023] Moreover, it is desirable that the water flow SV of the 1st non-reproducing mold ion exchange unit (space velocity) (SV1) and the water flow SV of the 2nd non-reproducing mold ion exchange unit (SV2) have the relation of $SV1 < SV2$ in the 2nd invention. This is from the reason processing with a film deaerator is desirable, after fully disassembling ozone, a hydrogen peroxide, etc. which generated the treated water of ultraviolet ray oxidation equipment for contact time by ultraviolet-rays oxidation by making it pass as a size comparatively to the 1st non-reproducing mold ion exchange unit.

[0024]

[Embodiment of the Invention] The flow Fig. showing the example of 1 operation gestalt of the ultrapure water equipments which drawing 1 - drawing 3 require for the 1st invention, respectively, drawing 4 - drawing 7 are the flow Figs. showing the example of 1 operation gestalt of the ultrapure water equipments concerning the 2nd invention, respectively. In drawing 1 - drawing 7, the same reference mark is given to the same component as the equipment of drawing 8, and the explanation is omitted. Moreover, in drawing 1 - drawing 7, a preprocessor system omits illustration and the primary pure drainage system system 8 has simplified illustration.

[0025] the equipment of drawing 1 is based on the secondary pure-water system 10 in the mixed bed of ultraviolet ray oxidation equipment 26 (shown all over [UV] drawing), and strongly acidic cation exchange resin and strongly basic anion exchange resin -- it installs so that it may let the non-reproducing mold ion exchange unit 40 (shown all over [CP] drawing) and the film deaerator 50 (shown all over [MD] drawing) of a type flow in this sequence 1 column.

[0026] The equipment of drawing 2 is replaced with the non-reproducing mold ion exchange unit 40 in the equipment of drawing 1, and the non-reproducing mold ion exchange unit 42 which prepared the entrance side and the mixed bed layer (shown all over [MB] drawing), strongly acidic cation exchange resin and strongly basic anion exchange resin, in the outlet side for the single flooring layer (shown all over [AER] drawing) of strongly basic anion exchange resin and which is a type 1 column is installed.

[0027] resin in the equipment of drawing 1, replace the equipment of drawing 3 with the non-reproducing mold ion exchange unit 40, and according to the single flooring of strongly basic anion exchange resin -- resin according a column 44

(shown all over [AER] drawing) to the mixed bed of a preceding paragraph side, strongly acidic cation exchange resin, and strongly basic anion exchange resin --- the column 46 (shown all over [MB] drawing) was established in the latter-part side --- the non-reproducing mold ion exchange unit 48 of a type is installed 2 columns.

[0028] The equipment of drawing 4 to the secondary pure-water system 10 Ultraviolet ray oxidation equipment 26 (shown all over [UV] drawing), it calls at the mixed bed of strongly acidic cation exchange resin and strongly basic anion exchange resin --- 1 column with the 1st non-reproducing mold ion exchange unit 40 (shown all over [CP] drawing) of a type it calls at the mixed bed of the film deaerator 50 (shown all over [MD] drawing), and strongly acidic cation exchange resin and strongly basic anion exchange resin --- it installs so that it may let the 2nd non-reproducing mold ion exchange unit 60 (shown all over [CP] drawing) of a type flow in this sequence 1 column.

[0029] in the equipment of drawing 4 , the equipment of drawing 5 is replaced with the 1st non-reproducing mold ion exchange unit 40, and is based on the single flooring of strongly basic anion exchange resin --- the ion exchange unit 70 (shown all over [AP] drawing) of a type is installed 1 column.

[0030] The equipment of drawing 6 is replaced with the 1st non-reproducing mold ion exchange unit 40 in the equipment of drawing 4 , and the non-reproducing mold ion exchange unit 42 which prepared the entrance side and the mixed bed layer (shown all over [MB] drawing), strongly acidic cation exchange resin and strongly basic anion exchange resin, in the outlet side for the single flooring layer (shown all over [AER] drawing) of strongly basic anion exchange resin and which is a type 1 column is installed.

[0031] resin in the equipment of drawing 4 , replace the equipment of drawing 7 with the 1st non-reproducing mold ion exchange unit 40, and according to the single flooring of strongly basic anion exchange resin --- resin according a column 44 (shown all over [AER] drawing) to the mixed bed of a preceding paragraph side, strongly acidic cation exchange resin, and strongly basic anion exchange resin --- the non-reproducing mold ion exchange unit 48 which established the column 46 (shown all over [MB] drawing) in the latter-part side is installed.

[0032] In addition, in the equipment of drawing 1 - drawing 7 , other equipments may be installed [between ultraviolet ray oxidation equipment and the non-reproducing mold ion exchange unit of the latter part] if needed between this film deaerator and the non-reproducing mold ion exchange unit of the latter part between this non-reproducing mold ion exchange unit and the film deaerator of the latter part.

[0033]

[Example] The underwater dissolved oxygen concentration in each point of the ultrapure water equipments shown in drawing 1 - drawing 7 , dissolved nitrogen concentration, and resistivity were measured. In this case, processing conditions were carried out as follows using the following as each equipment. moreover --- measurement of dissolved oxygen concentration --- DO[by Toa Electronics, Ltd.]-30A --- using --- measurement of resistivity --- the ORGANO CORP. make - MH-4 were used. A result is shown in Tables 2-8. In addition, in the ultrapure

water equipments shown in drawing 1 ~7, the dissolved oxygen concentration of the outlet water of the demineralizer 12 of the primary pure drainage system system 8 and vacuum deairing equipment 20 (refer to drawing 8) was 8.0 ppm and 24ppb, respectively.

[0034] Equipment and ultraviolet-ray-oxidation-equipment 26:TDFL-4 (product made from 1000 Shirota **** Co.)

- Ion exchange equipment 40 : Amberlite EG-4 (loam and product made from HASU)

- Ion exchange equipment 42 : Amberlite IRA-402BL+ Amberlite EG-4 and an ion exchange equipment 48: Amberlite IRA-402BL, Amberlite EG-4 and ion-exchange-equipment 70:Amberlite IRA-402BL and film deaerator 50:MJ-520p (Dainippon Ink & Chemicals, Inc. make)

- Ion exchange equipment 60 : Amberlite EG-4[0035] amount of UV irradiation: in a processing condition and ultraviolet ray oxidation equipment 26 — water flow SV:120hr-1[0036 in degree of vacuum:25Torr and the ion exchange unit 60 in water flow SV:50hr-1 and the film deaerator 50 in 0.3 Kw-hr/m3 and ion exchange units 40, 42, 48, and 70 —]

[Table 2]

図1の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppm)	抵抗率 ($\text{M}\Omega \cdot \text{cm}$)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(40)出口	1.0	1.2	18.2
膜脱気装置(50)出口	< 1	< 2	18.1

[Table 3]

図2の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppm)	抵抗率 ($\text{M}\Omega \cdot \text{cm}$)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(42)出口	1.0	1.2	18.2
膜脱気装置(50)出口	< 1	< 2	18.1

[Table 4]

図3の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppm)	抵抗率 ($\text{M}\Omega \cdot \text{cm}$)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(48)出口	1.0	1.2	18.2
膜脱気装置(50)出口	< 1	< 2	18.1

[Table 5]

図4の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppm)	抵抗率 ($\text{M}\Omega \cdot \text{cm}$)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(40)出口	1.0	1.2	18.2
膜脱気装置(50)出口	< 1	< 2	18.1
イオン交換装置(60)出口	< 1	< 2	18.2

[Table 6]

図 5 の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppb)	抵抗率 (MΩ・cm)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(70)出口	1.0	1.2	18.0
膜脱気装置(50)出口	< 1	< 2	17.9
イオン交換装置(60)出口	< 1	< 2	18.2

[Table 7]

図 6 の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppb)	抵抗率 (MΩ・cm)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(48)出口	1.0	1.2	18.2
膜脱気装置(50)出口	< 1	< 2	18.1
イオン交換装置(60)出口	< 1	< 2	18.2

[Table 8]

図 7 の装置

測定ポイント	溶存酸素濃度 (ppb)	溶存窒素濃度 (ppb)	抵抗率 (MΩ・cm)
純水貯槽(24)出口	2.2	1.2	17.5
紫外線酸化装置(26)出口	6	1.2	17.5
イオン交換装置(48)出口	1.0	1.2	18.2
膜脱気装置(50)出口	< 1	< 2	18.1
イオン交換装置(60)出口	< 1	< 2	18.2

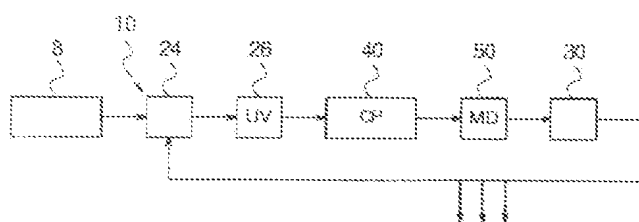
[0037] According to the 1st invention and the 2nd invention, Table 2 – 8 shows that each of dissolved oxygen concentration and dissolved nitrogen concentration can obtain very low ultrapure water. Moreover, according to the 2nd invention, it turns out that the ultrapure water from which the impurity was removed nearly completely can be obtained.

[0038]

[Effect of the Invention] As explained above, according to the ultrapure water equipments of the 1st invention and the 2nd invention, dissolved oxygen concentration is very low, and can obtain the ultrapure water which also reduced greatly the total dissolved gas concentration containing dissolved oxygen and dissolved nitrogen. Moreover, according to the ultrapure water equipments of the 2nd invention, an impurity can obtain the ultrapure water reduced more.

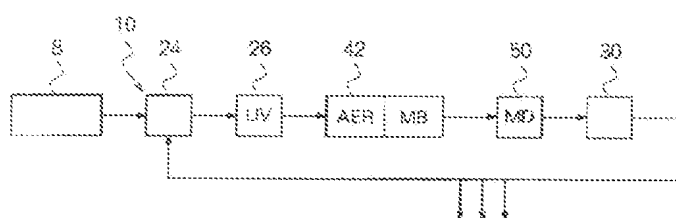
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Drawing selection drawing 1



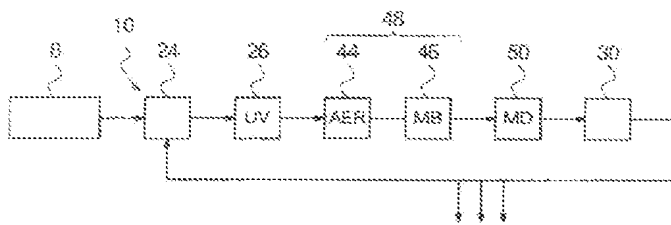
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Drawing selection drawing 2



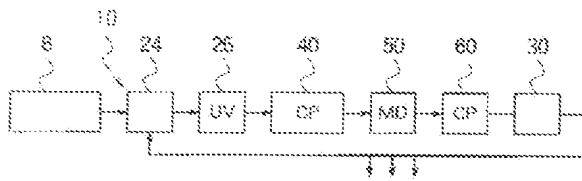
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Drawing selection drawing 3



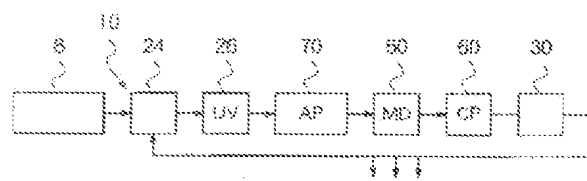
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Drawing selection drawing 4



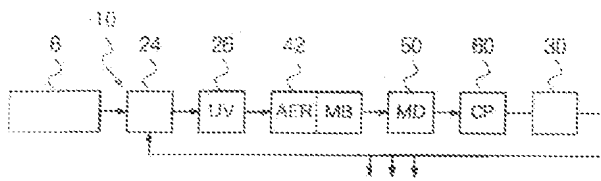
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Drawing selection drawing 5



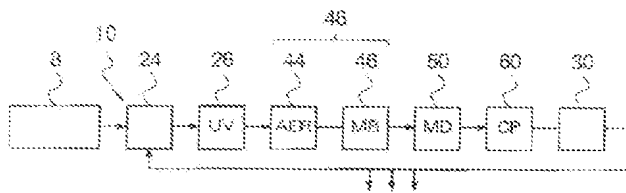
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Drawing selection drawing 6



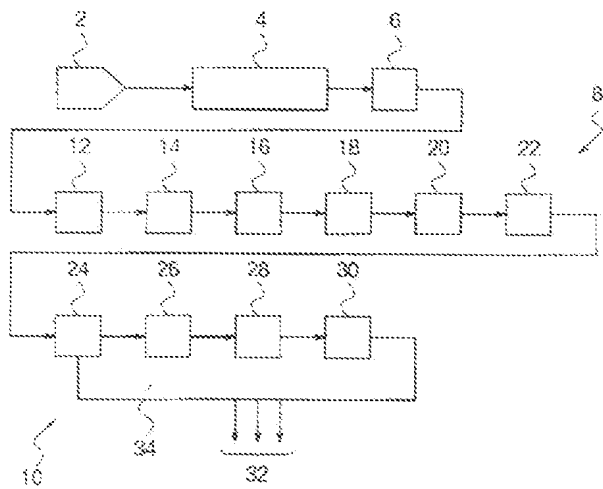
[Translation done.]

Drawing selection drawing 7



[Translation done.]

Drawing selection drawing 8



[Translation done.]